

First Principles NMR Signatures of Graphene Oxide

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Nuclear magnetic resonance (NMR) has been widely used in the graphene oxide (GO) structure study. However, the detailed relationship between its spectroscopic features and the GO structural configuration has remained elusive. Based on first principles ^{13}C chemical shift calculations using the gauge including projector augmented waves (GIPAW) method, we provide a spectrum-structure connection. Chemical shift of carbon is found to be very sensitive to atomic environment, even with an identical oxidation group. Factors determining the chemical shifts for epoxy and hydroxy groups have been discussed. GO structures previously reported in the literature have been checked from the NMR point of view. The energetically favorable hydroxy chain structure is not expected to be widely existed in real GO samples according to our NMR simulations. The epoxy pair we proposed previously is also supported by chemical shift calculations.

I. INTRODUCTION

Graphene has been the rising-star material in the past several years, due to its unique electron structure and its great application potential. [1–4] However, its large-scale production remains a big challenge. Reduction of graphene oxide (GO), which is obtained by oxidation and exfoliation of graphite, [5] provides a promising way to obtain graphene or chemically modified graphene massively. [6–9] Solution based chemical processes are expected to be applicable to many kinds of applications, which makes GO itself an important material. [10–15]

Despite a big effort from both experimentalists [9, 16–21] and theoreticians, [22–27] the precise chemical structure of GO is still not clear. The main reason for the difficulty to understand its structure is the amorphous and nonstoichiometric nature of GO. At the same time, different samples have different levels of oxidation, which makes things even more complicated. Nevertheless, some fundamental structural features of GO, as proposed by Lerf and coworkers, [19] have been widely accepted. In this so-called Lerf mode, hydroxy (-OH) and epoxy (-O-) groups spread across the graphene planes, while carboxylic acid groups (-COOH) exist at edge sites, possibly in addition to the keto groups.

Aside from this general picture, there are still many open questions about the GO structure. For example, how are the hydroxy and epoxy groups distributed on the GO plane? Do they aggregate together or avoid each other? Is there any other new species in GO, especially for highly oxidized samples? Are sp^2 carbon atoms clustered in aromatic forms?

It is very difficult to answer these questions based only on experimental raw data. Therefore, theoretical modeling has played an important role in GO structure study. Based on first principles energetics, many GO structure models have been proposed. Adapting a 2×2 unit cell,

Boukhvalov et al. [22] and Lahaye et al. [23] systematically studied the possible atomic configurations with different ratios of epoxides to alcohols at different degrees of oxidation. Based on a study with similar strategy, Yan et al. [25] emphasized that it is favorable in energy to form hydroxyl chains with hydrogen bonds. In a GO hydrogen storage study, Wang et al. [12] constructed a GO model with a building block which has the lowest energy at a very low oxidation group coverage.

Although it is very straightforward to conduct in theoretical study, the power of energetics analysis is expected to be limited by the complexity of the GO potential energy surface, especially when artificial periodic boundary condition must be adopted with a small unit cell. In contrast, computational spectroscopy provides information which can be directly compared with experiments. Therefore, it is a powerful alternative in nanostructure studies. For example, using Raman spectrum simulation, Kudin et al. [28] proposed an alternating single-double bond GO structure model. Recently, our x-ray photoelectron spectroscopy (XPS) simulation also led to a prediction of the epoxy pair and epoxy-hydroxy pair species in highly oxidized GO samples.[26]

Nuclear magnetic resonance (NMR) is the most widely used experimental technique in GO structure study. [9, 16–20] In fact, the popular Lerf model is mainly based on ^{13}C NMR experiments. [19] Currently, very high quality NMR spectrum is available via synthesis of almost fully ^{13}C -labeled GO. [20] There are mainly three broad resonances in the ^{13}C NMR spectrum of GO. By checking a series of reactions of GO with different reagents, the peak around 60 ppm is assigned to carbon atoms bonding to the epoxy group, and the peak around 70 ppm is corresponding to the hydroxy group connected carbon atoms. [19] The sp^2 carbon has a NMR peak at about 130 ppm. Besides the three main peaks, there are also three small peaks clearly shown in the high resolution ^{13}C NMR spectrum. [20] Gao et al. [9] suggested the these three peaks at 101, 167, and 191 ppm are corresponding to lactol, carboxy, and ketone groups, respectively. All these NMR assignments are based on chemical intuition, it is highly desirable to confirm them by first-principles

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simulations.

Theoretical NMR simulation has been widely used in studies of carbon nanotubes (CNTs). [29–34] ^{13}C NMR isotropic chemical shifts of pristine CNTs, based on the density functional theory (DFT) and an infinite CNT model, depend on the electronic structure and the diameter but not on the chirality. [31] It has also been demonstrated that a wealth of knowledge on functionalizations [32, 34] and defects [33] of CNTs can be obtained from NMR simulations. Similarly, new insights about GO structure are expected to be obtained by a systematic computational NMR study.

II. COMPUTATIONAL DETAILS

All of our calculations were performed with a plane wave based DFT implementation within the CASTEP package, [35, 36] and the gauge including projector-augmented plane-wave (GIPAW) method [39, 40] was used to calculate NMR shielding tensors. Ultrasoft pseudopotentials [37] were used to describe the interaction between valence electrons and ions. The revised Perdew-Burke-Ernzerhof (RPBE) density functional [38] used in this study has been demonstrated to be accurate enough for NMR simulation of CNTs. [30] The energy cutoff of plane wave basis set in our calculations was chosen to be high enough (500 eV) to converge energy, geometry, and nuclear shielding tensor.

When considering isolated oxidation groups, to avoid handling metallic system, we adopted an armchair graphene nanoribbon (AGNR) with a finite band gap as our substrate system. The vacuum space between two neighboring AGNRs was wider than 10 Å in both directions perpendicular to the ribbon direction (the z direction in Figure 1a). Along z direction, unless otherwise specified, a two-unit supercell (8.52 Å long according to the graphene lattice constant) was used to make sure that oxidation groups on the ribbon do not interact with their images in neighboring supercells. Atom coordinates of the functionalized ribbons were fully optimized while the supercell size was fixed. A $1 \times 1 \times m$ k -grid was used for Brillouin zone integration, and m was large enough to make the isotropic chemical shifts of all carbon atoms differ less than 1 ppm to those with a $1 \times 1 \times m-1$ grid.

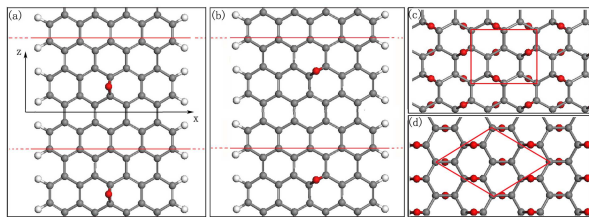


FIG. 1: An epoxy group adsorbs at (a) a P-site or (b) a D-site on 9-AGNR. (c) and (d) Two full-oxidized GO with epoxide only. Supercells used in our calculations are marked by red line. Carbon is in gray, oxygen in red, and hydrogen in white.

For highly oxidized GO samples, graphene based two dimensional (2D) models were used. And some special structure models proposed in previous energetics studies were taken for NMR calculations. We optimized both atom coordinates and cell parameters for all 2D models. The k -grid was also carefully tested to make sure that the NMR chemical shifts of all carbon atoms have converged.

As a commonly used method, the calculated ^{13}C chemical shift of benzene was used to calibrate the chemical shift for other systems, [29, 30] which generally leads to a quantitative agreement between theory and experiment. The isotropic chemical shift of benzene molecule calculated using a cubic cell of $15 \times 15 \times 10 \text{ Å}^3$ was 42.2 ppm, agreeing well with previous studies. [30] As an additional test, we calculated the chemical shift of a (7,0) CNT, and the result, 136.3 ppm, also agrees well with the value (136.4 ppm) obtained by Zurek et al.. [30]

III. RESULTS AND DISCUSSION

A. Epoxy groups

First, we consider an isolated epoxy group on an AGNR with 9 carbon chains (9-AGNR). The epoxy group can be attached to a C-C bond either parallel to the ribbon direction (P-site, Figure 1a) or diagonal to the ribbon direction (D-site, Figure 1b). C_E is used to name carbon atoms connecting to an epoxy group. The optimized C-C bond length between the two C_E carbon atoms is 1.50 Å for the P-site and 1.52 Å for the D-site, close to that of sp^3 hybridized carbon. For a P-site adsorbed epoxy group, chemical shifts of the corresponding two C_E atoms are both 68.0 ppm. [41] Due to its lower symmetry and the finite AGNR width, there is a small difference (less than 1.5 ppm) between the chemical shifts of the two C_E atoms in the D-site case. Their averages is 69.4 ppm. It is very interesting to note that the chemical shift of isolated epoxide group is close to the experimental peak value of hydroxy group around 70 ppm instead of 60 ppm assigned for epoxy group.

To check the width effect of the ribbon model, we have also tested wider AGNR with 10 carbon chains (10-AGNR). The corresponding C-C bond lengths are 1.50 and 1.53 Å for the P- and D-site, respectively. The average chemical shifts of the two C_E atoms are 67.2 and 73.2 ppm for these two adsorption sites. Their difference becomes larger than that of 9-AGNR, which may due to the 3-family behavior of the ANGR electronic structure. [42] However, the overall picture for 10-AGNR is the same as before, and chemical shifts close to 70 ppm are still obtained for individual epoxy groups.

It is interesting to see how the chemical shift changes upon the change of the epoxy group concentration. As another limit compared to the isolated epoxide case with the lowest concentration, we consider the fully epoxidized GO, which has the highest epoxy group concentration. Two fully-oxidized models with chemical formula C_2O

have been considered. Both have an optimized C-C bond length of about 1.50 Å. The first one (Figure 1c) has a C_E chemical shift of 59.8 ppm. The second one (Figure 1d) is part of a previously proposed GO structure model, [25] which leads to a C_E chemical shift of about 57.4 ppm. Therefore, the 100% functionalized graphene epoxide has a chemical shift close to the experimental value 60 ppm, which is much lower than that of isolated epoxides. ^{13}C chemical shift of epoxide in GO is thus very sensitive to chemical environment, and isolated epoxy groups should not be widely existed in the experimentally prepared GO samples.

B. Hydroxy groups

For single hydroxy groups, a four unit supercell along the ribbon direction with two hydroxy groups has been used to calculate their chemical shifts. [41] C_H is used to indicate carbon atoms connected to a hydroxy group. For 9-AGNR (Figure 2a), the C_H chemical shift of the isolated hydroxy groups is 72.4 ppm, close to the 70 ppm peak position in experiments. 10-AGNR gives a similar result, with a C_H chemical shift of 72.2 ppm.

Isolated hydroxy pairs have also been considered. Energetically, the most stable configuration has two hydroxy groups occupying a 1,2-site on two opposite sides of the graphene plane. P-site and D-site can be similarly defined as in the isolated epoxy group case. For 9-AGNR, the chemical shifts of the two C_H atoms are very close, and their averages are 72.2 and 72.0 ppm in the P-site (Figure 2b) and the D-site (Figure 2c) cases, respectively. Both values are close to 70 ppm assigned to hydroxy groups in experiment. The optimized C_H - C_H bond length is around 1.54 Å for both the P- and D-sites. Similar results are obtained for wider 10-AGNR, and the averaged C_H chemical shifts are 68.2 and 73.3 ppm for the P-site and D-site, respectively.

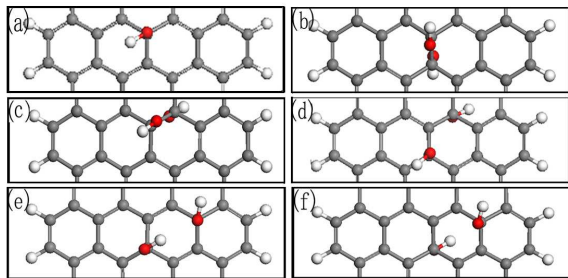


FIG. 2: (a) An isolated hydroxy group, (b) a P-site hydroxyl pair, (c) a D-site hydroxyl pair, (d) a 1,3- hydroxyl pair, (e) a 1,4-hydroxyl pair on the same side, and (f) a 1,4-hydroxyl pair on two opposite sides. Only part of the supercell used in calculations is shown.[41] Carbon is in gray, oxygen in red and hydrogen in white.

To further understand the chemical shift of isolated hydroxy pair, three other models have also been consid-

ered, where the two hydroxy groups occupy a 1,3-site on two opposite sides (Figure 2d), a 1,4-site on the same side (Figure 2e), or a 1,4-site on two opposite sides (Figure 2f). The 1,3-hydroxyl model with hydroxy groups on the same side is not stable after optimization. For 9-AGNR, the chemical shifts of the two C_H atoms in the opposite-side 1,3-hydroxyl case is close, and their average is 70.8 ppm. The 1,4-hydroxy groups on the same side lead to much lower chemical shifts, 64.3 ppm for the C_H atom closer to the ribbon edge and 63.0 ppm for the other C_H atom. If wider 10-AGNR is used, the corresponding chemical shifts are 67.1 and 64.5 ppm. For 1,4-hydroxy groups on two opposite sides, the averaged chemical shifts are 63.4 and 65.4 ppm for 9-AGNR and 10-AGNR, respectively.

Therefore, isolated hydroxy group and hydroxy pair in many cases give C_H chemical shifts around 70 ppm. But in some other cases (1,4-hydroxyl), it is also possible to obtain chemical shifts between 60-70 ppm. At the fully-oxidized limit, hydroxyl groups will bond to two opposite sides for each neighboring carbon atom pair. However, there is still a large repulsion between hydroxy groups. [43] The optimized C-C bond length is 1.64 Å, which is much larger than a normal C-C bond length and leads to an energetically very unfavorable structure. The calculated C_H chemical shift is 91.7 ppm.

C. Mixed epoxy and hydroxy groups

In real GO samples, both epoxy and hydroxy groups exist, and they are expected to be randomly distributed on the graphene basal planes. Therefore, a realistic GO model must include both epoxy and hydroxy groups and consider the interaction between them. For simplicity, we still start from the lowest concentration limit using ribbon models. Obtained structure motifs can be used as building blocks for a more realistic GO model with higher oxidation group concentration.

Based on energetics consideration, two stable local structures consisting both epoxide and hydroxyl have been proposed. [12] Here we adopt them in our ribbon model and name them structure A and structure B (Figure 3), respectively. When structure A is put on 9-AGNR at a D-site (Figure 3a), the chemical shifts of two C_E atoms are close, with an average of 56.4 ppm. The distance between the two epoxide carbon atoms is 1.47 Å, slightly shorter than those of isolated epoxide. Chemical shifts for the two C_H atoms are 66.4 and 70.5 ppm, with the one closer to ribbon edge 4.1 ppm larger. This trend is in agreement with isolated 1,4-hydroxyl pair. When structure A is located at a P-site (Figure 3b), the average C_E chemical shift is 58.2 ppm. The optimized C-C bond length in the epoxide is still 1.47 Å. The chemical shifts for the two C_H atoms are 69.3 and 65.5 ppm, with the up C_H about 4 ppm larger. This is possibly due to the hydrogen bond formed between the two hydroxy groups. Similar results have been obtained for 10-AGNR.

For structure B at a D-site (Figure 3c), chemical shifts of two C_E atoms are 62.2 and 69.1 ppm. While the chemical shifts of two C_H atoms are close, with an average of 70.5 ppm. Here, the bond length between two epoxide carbon atoms is 1.49 Å, and it is 1.56 Å between the two hydroxyl carbon atoms. For P-site (Figure 3d), the chemical shifts of the two C_E and two C_H atoms are close, and their averages are 62.8 and 69.2 ppm, respectively. The distance between two epoxide carbon atoms is 1.48 Å. Such a bond length slightly shorter than that of an isolated epoxide may be an indicator of lower chemical shift. In the 10-AGNR case, we get similar result for P-site, while for D-site, the chemical shift difference for two C_E atoms becomes much smaller, with an average chemical shift of 64.7 ppm. This result indicates that the big difference of the two C_E chemical shifts observed in 9-AGNR is not intrinsic.

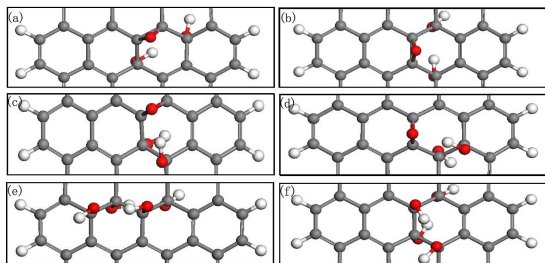


FIG. 3: Structure A locates at (a) a D-site or (b) a P-site in 9-AGNR. Structure B locates at (c) a D-site or (d) a P-site in 9-AGNR. Two hydroxyl pairs in (e) zigzag or (f) armchair directions. Only part of the supercell used in calculations is shown. Carbon is in gray, oxygen in red, and hydrogen in white.

Now, we have seen that, by adding proximate hydroxy groups, it is possible to decrease the chemical shift of epoxy group from about 70 ppm for isolated group towards the experimental value at 60 ppm. Therefore, in a realistic GO model, epoxy groups should be close to hydroxy and other epoxy groups. With higher oxidation group concentration, many GO structure models have been reported in the literature. [12, 22, 23, 25] We choose some typical structures for NMR simulations.

Based on a 2×2 supercell, Boukhvalov et al. [22] proposed the most stable structure of GO with a 75% coverage of oxidation groups. Their model (Figure 4a) has a chemical formulism of $C_8(OH)_4O$, and its unit cell is composed of a structure B unit and a 1,2-hydroxy pair. An important feature of the Boukhvalov model is that the hydroxy groups form chains, with hydrogen bonds forming within the chains, which is a main reason why such a structure is energetically very stable. The average chemical shifts of C_E and C_H are 66.8 and 76.8 ppm, respectively. Both are much larger than their experimental values. The C_E - C_E bond length is 1.51 Å, and the averaged length of C-C bonds in hydroxy chains is 1.58 Å, larger than that of isolated hydroxy pair. We find

that the hydroxyl molecules are the main reason of the wrinkling of carbon skeleton, as also suggested in a previous study. [23] When hydroxy groups form chains, it elongates the corresponding C-C bonds, which may then generate larger C_H chemical shifts.

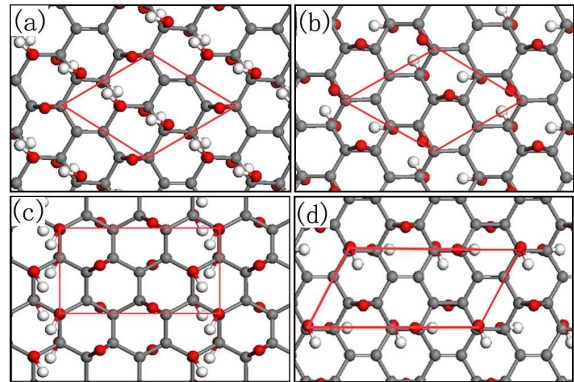


FIG. 4: Typical GO structure model proposed by (a) Boukhvalov et al., (b) Lahaye et al., (c) Yan et al., and (d) Wang et al.. The supercells used in our calculations are marked with red lines. Carbon is in gray, oxygen in red, and hydrogen in white.

With the same 2×2 supercell, calculations by Lahaye et al. suggest that too many hydroxy groups will lead to a too large tension. [23] Therefore, instead of $C_8(OH)_4O$, a GO model (Figure 4b) with a chemical composition $C_8(OH)_2O_2$ was suggested. In this model, hydroxyl molecules are attached to carbon atoms directly adjacent to epoxides, but at an opposite side of the carbon plane. Hydroxy groups do not form chains any more. Actually, this structure can be considered as a composition of a structure A unit and an additional epoxy group per unit cell. After optimization, the length of the bond between two epoxide carbon atoms is 1.49 Å, and the average length of the three C-C bonds connecting to a hydroxy group is about 1.54 Å. Our NMR calculations give an average C_E chemical shift of 60.6 ppm, and the chemical shifts of the two C_H carbon atoms are both 75.6 ppm. Compared to experiments, the 1,4-hydroxyl configuration adopted in this model leads to a too large chemical shift.

Based on a systematic energetics analysis, Yan et al. argued that all structures with a negative formation energy are fully oxidized GO with 1,2-hydroxyl pairs forming a chain-like structure and epoxy groups on remaining C atoms. [25] One example is $C_6(OH)_2O_2$ (Figure 4c), where 1,2-hydroxyl chains are along the armchair direction instead of the zigzag direction as in the Boukhvalov model. The distance between two C_E atoms is about 1.49 Å, and the average C_H - C_H bond length is 1.58 Å, similar to those in chains in the zigzag direction. The average C_E chemical shift is 61.9 ppm, close to the experimental value. While the average C_H chemical shift is still too large (78.5 ppm), since hydroxy groups form chains.

Another GO structure model is constructed based on the structure A building block. [12] As shown in Figure 4d, in this model, structure A units are connected along the armchair direction. Here, the ratio of $C(sp^2)/C(-O-)/C(-OH)$ is 1:1:1. The averaged C-C distance for epoxy groups is 1.49 Å, while that for hydroxy pairs is 1.57 Å. The average chemical shifts for C_E and C_H atoms are 61.1 and 73.8 ppm, respectively. This structure model gives the best agreement with NMR experiments among the several models we studied here. We note several important structure features of this structure: the proximity between hydroxyl and epoxide, 1,2-hydroxyl pairs but without forming a chain structure, and a balanced ratio between hydroxyl and epoxide groups.

D. sp^2 carbon

The chemical shift of sp^2 carbon is also very important, since it is an indicator of the distribution of this carbon species. The chemical shifts of sp^2 carbon in nanoribbon models, including clean AGNRs, are generally between 119-130 ppm, with most of them around 120-125 ppm. They are smaller than the experiment value (129-133 ppm), which may be due to the limited width of the nanoribbons considered in this study and the hydrogen atoms at the ribbon edges. For sp^2 carbon in an isolated C-C double bond surrounding by epoxy and hydroxy groups, we generally get a chemical shift much higher than the experimental value. All those GO models in Figure 4, which is not fully oxidized, have isolated C-C double bonds. The chemical shifts of isolated C-C double bonds are 143.4, 147.2, and 137.2 ppm for the model in Figure 4a, 4b, and 4d, respectively. Therefore, isolated sp^2 carbon pair is not the main form of sp^2 carbon in GO.

Yan et al. have suggested that a stable GO structure is composed of fully-oxidized regions like that shown in Figure 4b and sp^2 carbon strips between them. [25] Although their fully oxidized GO model gives too high C_H chemical shifts, our calculated results support their description on sp^2 C. For aromatic strips between fully oxidized regions, we obtain an averaged sp^2 chemical shift about 134 ppm, [41] which is in good agreement with experiments. We note that the large radius limit of the ^{13}C chemical shift of CNTs are much lower than 130 ppm. [31] Therefore, very large graphene area is also not expected to be existed in GO. This is consistent with the experimental cross peak between sp^2 C and epoxy/hydroxy groups in 2D NMR. [20] Finally, we reach the following picture about sp^2 carbon in GO: the main form of sp^2 carbon is small size aromatic clusters between highly oxidized regions.

E. Other oxidation groups

The assignment of the three small peaks in GO NMR spectrum is more difficult than that of the three strong resonances. Only recently, based on 1H - ^{13}C cross polarization (CP) spectrum, it was suggested that the 101 ppm signal is resulted from non-protonated carbons, [20] possibly a peripheral structure of GO containing five- and six-membered-ring lactols. [9] The 167 and 190 ppm peaks have been tentatively assigned to ketone and ester carbonyl, respectively. [9, 20]

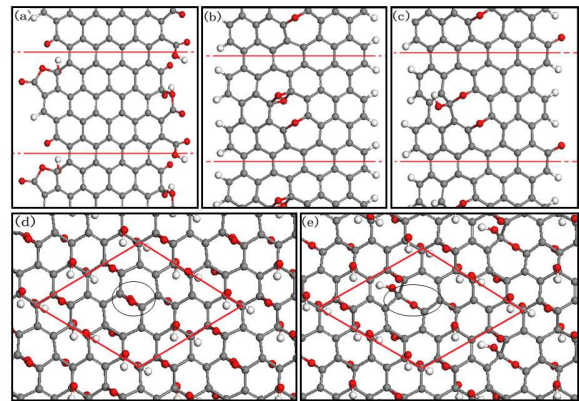


FIG. 5: (a) An AGNR model with 5- and 6-membered-ring lactols, carboxylic acid groups, and ketone groups. AGNR models with (b) an epoxy pair and (c) an epoxy-hydroxy pair. Two dimensional models with (d) epoxy pair and (e) epoxy-hydroxy pair. The unit cells used in our calculations are marked by the red line. Carbon is in gray, oxygen in red, and hydrogen in white.

To confirm those assignments reported in the literature, we construct an AGNR model (Figure 5a), which contains 5- and 6-membered-ring lactols, esters, carboxylic acid, and ketone groups. Chemical shifts of the sp^3 carbon atom in 5- and 6-membered-ring lactols are 104.9 and 96.9 ppm, respectively. Both are close to 101 ppm. The averaged chemical shift of $C=O$ is 191.6 ppm, which is also in agreement with the 190 ppm peak in previous assignments. However, we note that the chemical shift of $C=O$ can be strongly affected by its environment. For example, in Fig 5c, the edge $C=O$ group has a chemical shift only 173.1 ppm. The chemical shift of the edge carboxyl carbon is 162.2 ppm, close to 167 ppm peak in experiments. There is also a $COOH$ structure in 5- and 6-membered-ring lactols, which gives chemical shifts of 166.3 and 163.2 ppm respectively. Therefore, our calculations generally confirms previous assignment.

However, in a previous 2D NMR experiment, [20] cross peak has been observed for the 101 ppm peak, but not the other two minor peaks. Therefore, the 101 ppm peak is different in the three minor peaks. It may comes from on-plane groups instead of edge group. In a previous study, we have suggested that epoxy pair and epoxy-hydroxy pair may exist in highly oxidized GO samples. [26] It is

interesting to see what is their NMR signals. We use both ribbon model and 2D model to simulate their chemical shifts. Figure 5b shows an AGNR with an epoxy pair, where both carbon atoms bound by the epoxy pair have a chemical shift around 103.7 ppm. The chemical shift for epoxy-hydroxy pair in the ribbon model (Figure 5c) is 105.9 ppm. Bulk models give similar results, with a 101.4 ppm average chemical shift for epoxy pair (Figure 5d) and 106.8 ppm for epoxy-hydroxy pair (Figure 5e). Therefore, the NMR signal at 101 ppm strongly support the existence of epoxy pair we proposed in a previous cutting mechanism study [24] and XPS simulation. [26] Although its chemical shift is also close to 101 ppm, our results can not be used to support the existence of the epoxy-hydroxy pair, since the 101 ppm signal disappears in CP spectrum. [9]

F. Discussion

Isolated epoxide presents a C_E chemical shift around 70 ppm. It decreases to around 60 ppm in most cases, when epoxide is in close proximity with hydroxyl. A previous study [23] suggested that the sole presence of 1,2-ether epoxy group is not stable due to the accordingly created big tension on the carbon grid, and hydroxyl is needed to safe guard the stability of the structure. Therefore, the proximity of epoxy and hydroxy groups has both significant geometric effects and electronic effects. It's interesting to see whether the change of the chemical shift of the epoxy group is mainly a geometric or an electronic effect.

For this purpose, a computer experiment has been performed by calculating chemical shifts of an artificial system, which has the hydroxy groups taken off from a previously optimized geometry but fixing all other atoms. For the structure shown in Figure 3a, the average C_E chemical shift becomes 76.9 ppm after hydroxyl groups being taken off. For the structure in Figure 3b, the averaged C_E chemical shift also becomes 68.8 ppm, with obvious increase. Therefore, electronic effect plays an important role in the hydroxy induced chemical shift decrease of epoxide.

Our results suggest that hydroxy chain is not widely existed in GO, since its chemical shift is too high. To confirm this conclusion, we further consider the effect of nearby epoxy groups. Similar calculations have been performed by removing epoxy groups from the optimized geometries with hydroxy chains. For the structure shown

in Figure 4a, the average C_H chemical shift is 78.2 ppm after removal of epoxide, which is only 1.4 ppm larger than the original value. For the structure in Figure 4d, we also only get a 1.7 ppm chemical shift difference by removing the epoxy groups.

Therefore, the great geometrical distortions brought by the hydroxy chains should be the main reason of the chemical shift increase related to isolate hydroxy pairs. To see if there is any other effect, we consider two neighboring hydroxy pair. They can arrange along the zigzag direction (Figure 3e) or along the armchair direction (Figure 3f). In both cases, the C_H - C_H bond length is about 1.55 Å, much smaller than those in hydroxy chains. Therefore, the geometrical effect is small in these two cases.

In the zigzag direction case, the chemical shifts are 74.5, 67.2, 72.9, and 71.6 ppm for C_H carbon atoms from left to right, respectively. In the armchair case, the corresponding chemical shift is 74.1, 70.1, 70.4, and 74.2 ppm, from up to down. We can clearly see that the hydroxy group with a hydrogen bond pointed to it has a higher C_H chemical shift. Therefore, hydrogen bonding may also be an important factor in increasing the chemical shift of hydroxy group in hydroxy-pair chain.

IV. CONCLUSIONS

Our results are consistent with the Lerf model of GO, where the main species in GO are epoxide, hydroxyl, and sp^2 carbon. Their chemical shifts are very sensitive to their chemical environment, which leads to the result that peaks in GO NMR spectrum are very broad. When it is isolated, the chemical shift of epoxide is too high. Therefore, epoxide prefers to in close proximity with hydroxyl. Chemical shift of hydroxyl groups is closely related to its geometrical structure. Isolated 1,2-hydroxy pairs have stable chemical shifts around 70 ppm. However, when they form hydroxy chains, the chemical shift becomes much higher mainly due to the elongated C-C bonds. As a result, hydroxy chains widely proposed in literature based on energetics considerations should not be an important structure motif of GO. Our calculations also confirmed the existence of aromatic carbon clusters among highly oxidized regions. Considering its cross peak in 2D NMR, the small peak at 101 ppm is more likely contributed by on-plane groups, such as epoxy pair we proposed earlier.

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